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(54) Catalyst system for polymerising conjugated dienes

(57) The system comprises (A) a particular organo-aluminium compound, or aluminiumhydride, (B) a Lewis acid containing at least one halogen, and (C) a compound ML₃ where M is a lanthanide and L is a particular organic ligand. The use of the catalyst system gives polymers having high contents of 1,4-cis units.

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SPECIFICATION

Catalyst system for use in copolymerising diolefins

5 This invention relates to a catalyst system for use in homopolymerising and copolymerising diolefins.

Catalyst based on derivatives of rare earth metals are known for the polymerisation of unsaturated compounds. For example, the German Offenlegungsschrift No. 2,011,543 relates to the preparation of a catalytic system for the polymerisation of diolefins. The system is a ternary system consisting of (a) an organic compound of aluminium containing at least one C—Al bond, (b) an organometallic compound of a metal of Group IIIB of the Periodic Table (including the lanthanides), and (c) a compound containing one or more halide ions. The organometallic compound of the lanthanide is a co-ordination compound and contains organic ligands having from 1 to 20 carbon atoms. These ligands can be either monovalent and bidentate form, or bivalent and bidentate.

Furthermore, U.S. Patent Specification No. 3,641,188 describes a catalytic composition consisting of four components, namely (a) a compound of a lanthanide, (b) a reducing compound of aluminium, (c) a non-protonic Lewis acid and (d) a phosphine ligand. The compound of the lanthanide can be a co-ordination compound having a monodenate ligand. The catalytic system is used in the polymerisation of ethylenically unsaturated compounds to form polymers having an extremely low molecular weight, i.e. polymers containing not more than four monomer units.

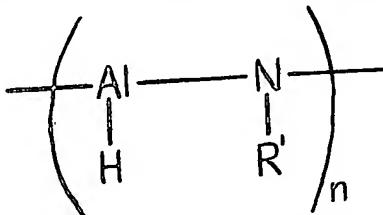
10 According to the present invention, there is provided a catalyst system comprising:

(A) either (i) an aluminium compound having the general formula RA_1XY , wherein R is a hydrogen atom or a hydrocarbon group containing from 1 to 20 carbon atoms, X is a hydrogen atom, a halogen atom, an alkoxy group, a thioalkoxy group or an amino group, Y is a hydrogen atom, a hydrocarbon group containing from 1 to 20 carbon atoms or a halogen atom, with the proviso that if X and Y are both halogen atoms, R is a 15 hydrogen atom, or (ii) a polymeric aluminium compound having the general formula:

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35 wherein R' is a hydrocarbon group containing from 1 to 20 carbon atoms and n is an integer;

(B) a Lewis acid containing at least one halogen atom; and

(C) a lanthanide compound having the general formula ML_3 , wherein M is the lanthanide and L is a monovalent monodentate ligand having the general formula $X'R''_p$, wherein X' is O, N, S or P, R'' is a hydrocarbon group containing from 1 to 20 carbon atoms, and p is an integer one less than the valency of X' .

40 The present invention also provides a process for the preparation of a polymer, which comprises polymerising one or more monomers at least one of which is a diolefin in the presence of a catalyst system according to the invention.

Examples of component (A) (ii) of the catalyst system are described in J. Organometal. Chem., 78, (1974), Ibid. 129, 281 (1977) and in the Patent Specifications cited above.

45 Component (B) of the catalyst system is a compound containing at least one halide ion. Such compounds can be indicated by the general name of "Lewis acid". Examples of component (B) of the catalyst system are (a) haloid acids; (b) halides of alkyl halides of metals of Group IIIA, and IVA, such as BC_1_3 , $A_1C_1_3$, $A_1C_1_3$, Et_2O , A_1Br_3 , A_1I_3 , O_9 , $A_1R_2C_1$ and $A_1RC_1_2$, in which R is an alkyl group containing from 1 to 20 carbon atoms; and (c) halides and alkyl halides of metals of Group IVBm VB and VIB, such as TiC_1_4 , VC_1_4 , MoC_1_6 and $CH_3TiC_1_3$.

50 Examples of the monovalent monodentate ligand L of component (C) of the catalyst system are alcoholic groups ($-OR_1$), dialkylamino groups ($-NR_1R_2$), thioalcoholic groups ($-SR_1$) and phosphinic groups ($-PR_1R_2$) wherein R_1 and R_2 , which are the same or different, are alkyl, cycloalkyl, aryl groups containing from 1 to 20 carbon atoms. Examples of component (C) are tri-alcoholates of lanthanides ($Ln(OR_1)_3$), trialkylamides of lanthanides ($Ln(NR_1R_2)_3$), tris-thioalcoholates of lanthanides ($Ln(SR_1)_3$), and dialkyl phosphinates of lanthanides ($Ln(PR_1R_2)_3$).

55 As is known, lanthanides are the elements of atomic numbers 57 to 71 inclusive. The preferred lanthanides for use in the invention are lanthanum, praseodymium, neodymium, samarium, gadolinium and dysprosium.

A characteristic feature of the catalytic system of the invention is that it results in polymers which usually have a high content of 1,4-cis units and molecular weights and molecular weight distributions variable over a wide range. Accordingly, there can be produced polymers with properties which are adapted to their intended use.

It is known that the properties of diene elastomers having a 1,4-cis structure are a function of their steric purity, their distribution of molecular weights, their mean molecular weight.

65 It is known that a few synthetic elastomers, namely poly(1,4-cis-isoprene) and poly(1,4-cis-butadiene),

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can crystallise due to the effect of heavy applied stresses (drawing). The occurrence of crystallinity leads to a self-reinforcement effect of the material, with a considerable improvement of its mechanical properties such as tensile strength and tear-resistance. (Thor, L. et al., Polymer Engineering and Science, 17, 129 (1977)).

The ability to crystallise and the magnitude of the crystallisation are a function of the content of 1,4-cis 5 units of the polymer, that is to say, of its stereo-regularity. In addition the temperature at which the elastomer 5 crystallises is a function of such stereoregularity.

Poly(1,4-cis-isoprene) has a favourable behaviour as regards crystallisation, that is, has a tendency to crystallise under a pulling stress at comparatively high temperatures. In the case of poly(1,4-cis-butadiene), crystallisation takes place at room temperature only when the content of 1,4-cis units is very high (L. Gargani 10 et al., Angew Makrom. Chem., 50, 101, (1976)). There is, thus, a practical interest in making a butadiene 10 polymer which is totally 1,4-cis since it would crystallise under a pulling stress at temperatures higher than ambient temperatures. This property is commonly a prerequisite in many applications, such as pneumatic tyres.

Summing up, the structural prerequisites for a good crystallizable elastomer are a high tacticity of the 15 macromolecules in order that a sufficient degree of crystallisation under drawing may be achieved; and an appropriate melting point temperature, situated in the temperature range at which the elastomer is required to work from the point of view of its practical application. 15

The most desirable molecular weight distribution depends upon the intended application of the polymer. In general, if the elastomer is to be processed by roll mills or by extruders, it is desirable to have a wide 20 distribution (e.g. a ratio of the weight average molecular weight to the numerical arithmetic mean molecular weight (M_w/M_n) higher than 4,) because it improves the extrudability and the capability of efficiently dispersing the compounding ingredients (M. Tokita et al., Rubber Chem. and Technol., 46, 1166 (1973)). 20

If, however, it is desired, for example, to dissolve the polymer in a solvent (such as in the production of anti-shock polystyrene in the "in mass" process, or in the production of certain types of adhesives), it is an 25 advantage to have a polymer with a narrow distribution (e.g. M_w/M_n in the range from 1 to 2) since the polymer dissolves in a short time without the formation of gelled particles, such formation being due to the high molecular weight fraction, this fraction being absent in this case. 25

The average molecular weight of an elastomer has an opposite effect upon its processability and its 30 stress-strain properties. As the molecular weight is increased, the processability is worsened whereas the stress-strain properties are improved. Thus, for good processability of an elastomer on a roller mill or an 30 extruder, the average molecular weights are of the order of magnitude of 0.3×10^{-6} to 0.6×10^{-6} . These values ensure the best admixture of the ingredients. 30

On the contrary, good mechanical properties, such as low heat build-up of an elastomer are obtained with 35 high average molecular weights. In fact, the number of molecular chain ends, which number decreases as the molecular weight increases, is one of the decisive factors in the dissipation of mechanical energy in the form of heat. (M. Bruzzone et al., IV Int. Synth. Rubber Stamp., London, September 10, 1969). Elastomers with a high molecular weight, say of 10^6 and over, are thus required in all the uses for which a low heat 35 build-up is necessary. Polymers with so high a molecular weight are used also to form oil-extended polymers.

40 By way of conclusion, as outlined above, the catalytic system of the invention permits one to produce elastomers having a very high steric purity and which are tailored to their intended use as regards their molecular weights and the distribution thereof. 40

The diolefins which can be polymerised in the presence of the catalytic systems of the invention include 45 aliphatic conjugated diolefins such as 1,3-butadiene, 1-substituted butadienes (e.g. 1,3-pentadiene), 2- substituted butadienes (e.g. isoprene), 2,3-substituted butadienes (e.g. 2,3-dimethyl-1,3-butadiene), and 45 their mixtures. 45

The catalyst system can be prepared in the presence or absence of the monomer to be polymerised. The particular procedure used has no decisive bearing upon the polymerisation. If no monomer is present, the preparation of the catalyst is generally carried out by adding to an aliphatic hydrocarbon solvent, a cycloaliphatic solvent, or an aromatic solvent, firstly the lanthanide compound such as $Nd(O-isoC_3H_7)_3$, secondly the organic aluminium compound such as $A_1(isoC_4H_9)_3$, and thirdly the Lewis acid such as A_1Br_3 . His sequential order is not essential. 50

The same order can be used also for catalyst systems prepared "in situ". The components of the catalytic system can be added separately from the diolefin to be polymerised, the latter being dissolved in the 55 reaction solvent. It is possible, moreover, to effect the preparation "in situ" by employing small amounts of the diolefin to be polymerised (e.g. with molar ratios of the diolefin to the lanthanide of between 5 and 50).

The proportions of the components of the catalyst system can be varied within a wide range. The molar ratio of the organic aluminium compound (component A) to the lanthanide compound (component C) is preferably from 1 to 120. The atomic ratio of the halide ions to the lanthanide is preferably from 0.1 to 10, 60 more preferably from 0.8 to 4. 60

An interesting aspect of the catalyst system of the invention is its high activity. The amount of catalyst system used can thus be very low, and is a function of the purity of the reagents which are employed. Depending upon the purity, the amount of catalyst system normally used is from 0.015×10^{-3} to 0.5×10^{-3} gramatoms of lanthanide per 100 grams of monomer. 65

65 Polymerisation can be carried out either in the presence of aliphatic, aromatic and cycloaliphatic hydrocar-

bon solvents, or in the presence of the monomer alone (mass polymerisation). By using mass polymerisation, extremely short reaction times are attained, of the order of a few minutes with a complete conversion and viscometric molecular weights of the polymer obtained of the order of 2×10^6 to 3×10^6 . This means that chain-transfer reactions with the monomers are very poorly operative when the catalyst systems of the invention are used, this is quite unusual for this kind of catalysis.

The polymerisation is preferably carried out at a temperature of from -50°C to 150°C , more preferably from 10°C to 80°C , and at a pressure of from 1 to 10 atmospheres, more preferably from 1 to 5 atmospheres. The pressure is generally provided by the vapor pressure of the monomer(s) under the working conditions which are used.

10 The polymers obtained usually have a high contents of 1,4-cis units. Values higher than 99% can be attained with butadiene.

The intrinsic viscosity, as measured in toluene at 30°C , of the polymers obtained is usually from 2 to 16 dl/g, depending upon the conditions which have been used.

15 The distribution of molecular weights, in terms of the Mw/Mn ratio, may vary within a wide range, depending upon the requirements as to the practical use of the polymers.

15 The polymers usually are virtually gel-free, and soluble in common solvents, even when the molecular weight is high.

The invention will now be illustrated by the following Examples. In some of the Examples, the following Procedures A and B were used.

20 Procedure A
In a pop bottle having a capacity of 200 ml and which had previously been purged with an inert gas, there

were introduced, under a nitrogen blanket, the solvent and then, in the order given, the organic aluminium compound (A), the diolefin, the lanthanide compound (C) and the Lewis acid (B). To carry out polymerisation, the bottle was placed in a rotary bath, the temperature of which was thermostatically controlled at the selected temperature, for the necessary time. On completion, the bottle was opened and the contents were

25 poured into 500 ml of methanol containing 1% of a phenolic antioxidant. The coagulated polymer was dried in vacuum at room temperature overnight, and was then ready for analysis.

Procedure B
A glass reactor equipped with a water-jacket, an anchor stirrer and sump valve on the bottom of vessel, was

30 charged, with stirring and under a nitrogen stream, with the solvent and the diolefin to be polymerised. By means of the jacket, the internal temperature was brought to the desired value, whereafter there were introduced, in the order given, the organic aluminium compound (A), the lanthanide compound (C) and the Lewis acid (B). The contents of the reactor were stirred and kept at the desired temperature and, after the necessary time, the contents were allowed to flow through the sump valve into a vessel containing

35 methanol. The coagulated polymer was dried in an oven and weighed, and was then analysed.

EXAMPLES 1 to 4

By using procedure A above, butadiene was polymerised in the presence of a catalyst system including alcoholates of various lanthanides. The conditions used and results obtained are tabulated in Table 1 below.

EXAMPLES 5 to 9

40 By using procedure A above, butadiene was polymerised in the presence of a catalyst system including various alcoholates of neodymium. The results obtained are tabulated in Table 2 below.

EXAMPLES 10 to 14

45 By using procedure A above, butadiene was polymerised in the presence of a catalyst system including neodymium alcoholates and various Lewis acids. Table 3 below gives the conditions used and the results obtained.

EXAMPLE 15

A 200 ml pop bottle, which had previously been purged with an inert gas and stoppered with a neoprene gasket and a perforated crown cap, was charged by a hypodermic needle soldered to a metal bottle with 51.8 g of liquid butadiene. By means of a metal syringe fitted with a hypodermic needle there were introduced in

50 the order given:

- 0.24 ml (0.24 millimol) of a solution of isobutylaluminium monohydride (DIBAH) in hexane;
- 0.26 ml (0.006 millimol) of a solution of Nd(O-n-C₁₀H₂₁)₃ in hexane; and
- 0.20 ml (0.012 millimol) of a solution of A1EtC₁₂ in hexane.

The pop bottle was placed in a rotary bath at 20°C for 5 hours. On completion of polymerisation, the bottle was opened and its contents were coagulated with 0.51 of methanol and dried in a vacuum oven. There were

55 obtained 39.5 g (yield 76.2%) of a polymer having the following properties:

1,4-cis content = 98.8%

$[\eta]_{30^\circ\text{C}} = 5.2 \text{ dl/g}$

toluene

60 Tm = + 1.5°C (Tm is the melting point temperature as measured with a Differential Scanning Colorimeter (DSC)).

EXAMPLE 16

A 200 ml pop bottle, which has been purged with nitrogen was charged, in the order given, with:

- 100 mls of Isoprene (68g);

65 (b) 0.5 ml (0.25 millimol) of a solution of A1(isoBu)₃ in hexane;

- (c) 0.5 ml (0.25 millimol) of a solution of Nd(O-n-Bu)₃ in hexane; and
 (d) 0.5 ml (0.04 millimol) of a solution of A1EtC₁₂ in hexane.

The pop bottle was stoppered and placed in a rotary bath at 50°C for 3 hours. On completion of polymerisation, the polymer obtained was coagulated with methanol and dried in a vacuum oven. There were obtained

5 26 g (yield 38.2%) of a polymer having the following properties:

1,4-cis content = 96.5%
 3,4 content = 3.5%

EXAMPLE 17

By procedure A above, butadiene and isoprene were copolymerised in hexane at 40°C for 2 hours, by 10 employing:

Hexane 100 ml
 Butadiene 10 g
 Isoprene 11.5 g
 A1(isoBu)₂H 0.31 millimol
 15 Nd(O-n-Bu)₃ 0.026 millimol
 A1EtC₁₂ 0.052 millimol

Coagulation with methanol was carried out, followed by drying. There were obtained 20.4 g (yield 95%) of a copolymer having the following properties:

Butadiene units in the copolymer = 48% (1,4-cis content = 98%)
 20 Isoprene units in the copolymer = 52% (1,4-cis content = 95%).

EXAMPLES 18 to 32

In Examples 18 to 28, polymerisation of butadiene was carried out by procedure A above, whereas in Examples 29 to 32, the polymerisation of butadiene was carried out by procedure B above. The reactants used and the results obtained are given in Table 4 below. Table 4 shows that the weight mean molecular 25 weight (M_w) varied between values of 300,000 and 2,000,000 and that the ratio of the weight mean molecular weight to the arithmetic mean molecular weight ($M_w : M_n$) varied between values of 2.7 and 19.

EXAMPLES 33 to 35

According to the procedure B above, butadiene was polymerised in the presence of a catalyst system including neodymium alcoholates. Table 5 below gives both the conditions used and the results obtained. It 30 can be seen that the activity of the catalyst system (in terms of gramatoms of neodymium per 100 grams of diolefin) is good.

EXAMPLE 36

A 200 ml pop bottle which had been purged with an inert gas, was charged, under a nitrogen blanket, with 100 ml anhydrous n-hexane and then, in the order given, with 0.05 millimol of Nd(O-isoC₃H₇)₃, 0.5 millimol 35 of A1(isoC₄H₉)₃ and 0.058 millimol of A1Br₃. Thus, the molar ration of component A to component C of the catalyst system is 10, and the molar ration of halogen to neodymium is 3.48.

The bottle was sealed with a neoprene gasket and a crown cap which is perforated so as to permit the introduction of a hypodermic needle. Then, through the hypodermic needle directly soldered to a metal bottle which contains anhydrous butadiene, there were introduced into the pop bottle 10.5 g of liquid 40 butadiene. The bottle was then placed on a rotary bath, thermostatically controlled at 30°C, for 2 hours to effect the polymerisation of butadiene. On completion, the bottle was opened and its contents poured into 500 ml of methanol which contained 1% of a phenolic antioxidant. The coagulated polymer was vacuum dried at room temperature overnight. The yield of solid polymer was 7.5 g, which corresponds to 71.4% of the monomer used. Infrared analysis carried out on a sample dissolved in CS₂ showed that it had a 1,4-cis 45 content of 98.5%, a 1,4-trans content of 1.4% and a 1,2 content of 0.1%.

Its intrinsic viscosity, measured at 30°C in toluene, was 4.25 dl/g. The melting point temperature of the polymer measured in a Differential Scanning Calorimeter, was 0°C.

EXAMPLE 37

Using the same procedure as in Example 36, the bottle was charged with 100 ml of n-hexane, 0.1 millimol 50 of Nd(O-iso-C₃H₇)₃, 1 millimol of A1(isoC₄H₉)₃, 0.17 millimol of A1EtC₁₂ and 30 g of butadiene, corresponding to the following ratios:

Molar ration of component A to component C = 10; and
 Atomic ratio of halogen to Nd = 3.4.

The polymerisation was carried out at 20°C for 4 hours. The results were as follows:

55 Dry polymer obtained : 28 g (93% of theory)
 Infrared analysis : 1,4-cis = 98.4%; 1,4-trans = 1.1%; 1,2 = 0.5%

$[\eta]_30 = 4.25 \text{ dl/g}$

toluene

50 T_m (D.S.C.) = -1°C
 $M_{visc} = 0.52 \times 10^6$

$M_{osm} = 0.37 \times 10^6$

Tensile strength (ASTM D-412) = 210 kg/cm²

Elongation at break (ASTM D-412) = 550%

Modulus at 300% elongation (ASTM D-412) = 100 kg/cm².

EXAMPLE 38

Using the same procedure as in Example 36, the bottle was charged with 180 ml of n-heptane, 2.0 millimols of A1(isoC₄H₉)₃, 0.010 millimol of Nd(O-n-C₃H₇)₃, 0.066 millimol of A1Br₃, and 20.2 g of butadiene, corresponding to a molar ratio of component A to component C of 20 and to an atomic ratio of halogen to neodymium of 1.98. Polymerisation was carried out at 50°C for 45 minutes. There were obtained 5.6 g of polymer, equal to 55% of the monomer used.

Infrared analysis: 1,4-cis = 97.0%; 1,4-trans = 2.6%; 1,2 = 0.4%.

EXAMPLE 39

A glass reactor equipped with water jacket, an anchor stirrer and a dumping valve on the bottom was charged, with stirring and under a nitrogen stream, with 7.7 litres of anhydrous hexane, 21 millimol of A1(isoC₄H₉)₃, 1.92 millimol of Nd(O-n-C₄H₉)₃, and 1.28 millimol of A1Br₃, corresponding to a molar ratio of component A to component C of 11 and to an atomic ratio of halogen to neodymium of 2. Then 420 g of butadiene and introduced through a stopcock connected by stainless tubing to the reactor and to a metal bottle containing liquid butadiene. The reactor contents were kept stirred at 25°C and water was circulated in the water-jacket. After 3 hours the contents of the reactor were allowed to flow through the bottom valve into a container full of methanol. The coagulated polymer was oven dried and weighed. There were obtained 395 g of solid polymer, equal to 94% of the monomer used.

Infrared analysis: 1,4-cis = 98.7%; 1,4-trans = 1.1%; 1,2 = 0.2%

$[\eta]_{30} = 5.8 \text{ dl/g}$
 toluene
 $M_{viscom} = 0.8 \times 10^6$
 $M_{osmotic} = 0.3 \times 10^6$
 Mooney value ML(1+1) 100°C = 91.5.

EXAMPLE 39

A glass reactor fitted with a water-jacket, anchor stirrer and a discharge valve on the bottom, was charged, with stirring and under a nitrogen stream, with 7.7 litres of anhydrous n-hexane, 21 millimols of A1(isoC₄H₉)₃, 1.92 millimol of Nd(O-n-C₄H₉)₃, and 1.28 millimol of A1Br₃, corresponding to a molar ratio of component A to component C of 11 and to an atomic ratio of halogen to neodymium of 2. Then 420 g of butadiene were introduced through a stopcock connected to the reactor by a stainless steel tube and to a small metal bottle which contained liquid butadiene.

The contents of the reactor were kept stirred at a temperature of 25°C, water being circulated through the water jacket. After 3 hours the contents of the reactor were allowed to flow through the bottom valve into a vessel containing methanol. The coagulated polymer was oven dried and weighed. There were obtained 395 g of a solid polymer, corresponding to 94% of the monomer used.

Infrared analysis: 1,4-cis = 98.7%; 1,4-trans = 1.1%; 1,2 = 0.2%.
 $[\eta]_{30} = 5.8 \text{ dl/g}$.
 toluene
 $M_{viscom} = 0.8 \times 10^6$
 $M_{osmotic} = 0.3 \times 10^6$
 Mooney value ML(1+1) 100°C = 91.5.

EXAMPLE 40

Using the same procedure as in Example 39, there were introduced into the reactor 7.5 litres of n-hexane, 21.0 millimols of A1(isoC₄H₉)₃, 1.92 millimol of Nd(o-n-C₄H₉)₃, 1.29 millimol of A1EtC₁₂ and 390 g of butadiene, the molar ratio of component A to component C being 11 and the atomic ratio of halogen to neodymium being 1.34. Polymerisation was carried out at 25°C for 3 hours. There were obtained 312 g (yield 80%) of solid polymer.

Infrared analysis: 1,4-cis = 98.8%; 1,4-trans = 1.0%; 1,2 = 0.2%

$[\eta]_{30^\circ\text{C}} = 5.3 \text{ dl/g}$.

toluene

EXAMPLE 41

Using the procedure of Example 39, the reactor was charged with 7.6 litres of n-hexane, 397 g of butadiene, 21.0 millimols of A1(iso-C₄H₉)₃, 1.92 millimol of Nd(O-n-C₁₀H₂₁)₃ and 1.28 millimol of A1Br₃, corresponding to a molar ratio of component A to component C of 10.9 and to a molar ratio of halogen to neodymium of 2.0. Polymerisation was carried out at 25°C for 3 hours. There were obtained 390 g (yield 98.5%) of solid polymer.

$[\eta]_{30^\circ} = 5.8 \text{ dl/g}$.

toluene

EXAMPLE 42

Using the procedure of Example 36, the pop bottle was charged with 100 ml of hexane, 31 g of butadiene, 0.1 millimol of Nd(O-n-C₁₀H₂₁)₃, 0.25 millimol of A1EtC₁₃ and, lastly, as component A, 0.042 of ene(N-isopropyliminoalene) [(HA1N-isoc₃H₇)₆], corresponding to 0.5 milligramatoms of aluminium. The bottle was sealed and polymerisation was carried out for 6 hours at 50°C. There are obtained 24.8 g of dry polymer.

Infrared analysis: 1,4-cis = 98.0%

$[\eta]_{30^\circ} = 8.7 \text{ dl/g}$.

toluene

TABLE 1

	Ex.	Solvent mls	Diolefin grams	Component A millimols	Component C millimol	Component B millimol	
5	1	Hexane 100	Butadiene 20	Al(Bu ⁱ) ₃ 0.75	Nd(OBu ⁿ) ₃ 0.05	AlBr ₃ 0.05	5
10	2	Hexane 100	Butadiene 20	Al(Bu ⁱ) ₂ H 1.5	Gd(OBu ⁿ) ₃ 0.05	AlEtCl ₂ 0.075	10
15	3	Hexane 100	Butadiene 20	Al(Bu ⁱ) ₃ 0.75	Dy(OBu ⁿ) ₃ 0.05	AlEtCl ₂ 0.075	15
20	4	Hexane 100	Butadiene 20	Al(Bu ⁱ) ₃ 1.5	Pr(OBu ⁿ) ₃ 0.05	AlBr ₃ 0.07	20
		Polymerization temperature °C	Polymerization time hrs.	Yield %	1,4-Cis %		
25		30	2	97	98.1		25
30		40	4	80	97.8		
		40	2	82	98.0		30
		40	2	60	98.0		

TABLE 2

	Ex.	Solvent mls	Diolefin grams	Component A millimols	Component C millimols	Component B millimols	
35	5	Hexane 100	Butadiene 30	Al(Bu ⁱ) ₃ 1.0	Nd(OPr ⁱ) ₃ 0.1	AlEtCl ₂ 0.17	35
40	6	Hexane 80	Butadiene 20.2	Al(Bu ⁱ) ₃ 2.0	Nd(OPr ⁿ) ₃ 0.1	AlBr ₃ 0.066	40
45	7	Hexane 100	Butadiene 12	Al(Bu ⁱ) ₃ 0.5	Nd(OC ₆ H ₁₁) ₃ 0.05	AlBr ₃ 0.05	45
50	8	Hexane 80	Butadiene 10	Al(Bu ⁱ) ₃ 0.5	Nd(OBu ⁿ) ₃ 0.04	AlEtCl ₂ 0.08	50
55	9	Hexane 80	Butadiene 9.6	Al(Bu ⁱ) ₃ 0.5	Nd(O ⁿ -C ₁₀ H ₂₁) ₃ 0.04	AlEtCl ₂ 0.06	55
		Polymerization temperature °C	Polymerization time hrs.	Yield %	1,4-Cis %		
60		30	3	93	98.4		60
		30	2	85	97.8		

		30	1	87	98.6	
5		30	0.4	90	98.0	5
		30	0.4	76	98.0	
10	Ex.	Solvent mls	Diolefin grams	Component A millimols	Component C millimols	Component B millimols
15	10	Hexane 80	Butadiene 9	Al(Bu ¹) ₃ 0.5	Nd(OBu ⁿ) ₃ 0.04	AlBr ₃ 0.047
	11	Hexane 80	Butadiene 8.5	Al(Bu ¹) ₃ 0.5	Nd(OBu ⁿ) ₃ 0.04	AlJ ₃ 0.033
20	12	Hexane 80	Butadiene 9	Al(Bu ¹) ₃ 0.5	Nd(OBu ⁿ) ₃ 0.04	AlEtCl ₂ 0.08
	13	Hexane 80	Butadiene 8.7	Al(Bu ¹) ₃ 0.5	Nd(O-nC ₁₀ H ₂₁) ₃ 0.04	AlBr ₃ 0.04
25	14	Hexane 80	Butadiene 8.8	Al(Bu ¹) ₃ 0.5	Nd(O-nC ₁₀ H ₂₁) ₃ 0.04	AlEtCl ₂ 0.07
30	Polymerization temperature °C		Polymerization time hrs.	Yield %	1,4-Cis %	30
		30	0.4	88	98.2	35
35		30	0.4	50	98.1	
40		30	0.4	90	98.0	40
		30	0.4	90	98.1	
45		30	0.4	70	98.4	45

TABLE 4

50	Ex.	Solvent mls	Diolefin grams	Component A millimol	Component C millimol	Component B millimol	50
55	18	Hexane 200	28.4	TIBA* 1.8	Nd(O-nC ₁₀ H ₂₁) ₃ 0.018	AlEtCl ₂ 0.018	55
	19	Hexane 200	31.1	TIBA 1.44	Nd(O-nC ₁₀ H ₂₁) ₃ 0.018	AlEtCl ₂ 0.045	
60	20	Hexane 100	10.8	TIBA 0.65	Nd(OBu ⁿ) ₃ 0.0065	AlEtCl ₂ 0.013	60
	21	Hexane 200	28.2	DIBAH** 1.17	Nd(O-nC ₁₀ H ₂₁) ₃ 0.018	AlEtCl ₂ 0.018	

TABLE 4 (continued)

	Ex.	Solvent mls	Diolefin grams	Component A millimols	Component C millimols	Component B millimols	
5	22	Hexane 200	28.5	DIBAH 0.72	Nd(OBu ⁿ) ₂ 0.018	AlEtCl ₂ 0.036	5
10	23	Hexane 200	28.8	TIBA 0.90	Nd(O-nC ₁₀ H ₂₁) ₃ 0.018	AlEtCl ₂ 0.036	10
	24	Hexane 200	28.4	TIBA 0.37	Nd(O-nC ₁₀ H ₂₁) ₃ 0.0123	AlEtCl ₂ 0.0185	
15	25	Hexane 200	29	TIBA 0.36	Nd(O-nC ₁₀ H ₂₁) ₃ 0.018	AlEtCl ₂ 0.045	15
	26	Hexane 200	28.4	TIBA 0.36	Nd(OBu ⁿ) ₃ 0.018	AlEtCl ₂ 0.036	
20	27	Hexane 200	28.5	DIBAH 1.17	Nd(OBu ⁿ) ₃ 0.018	AlEtCl ₂ 0.036	20
25	28	Hexane 200	28.5	DIBAH 1.8	Nd(OBu ⁿ) ₃ 0.018	AlEtCl ₂ 0.036	25
	29	Hexane 1500	402	TIBA 13.3	Nd(OBu ⁿ) ₃ 0.38	AlEtCl ₂ 0.76	
30	30	Hexane 3800	376	DIBAH 6.58	Nd(OC ₁₀ H ₂₁) ₃ 0.22	AlEtCl ₂ 0.438	30
	31	Hexane 1700	170	DIBAH 2.94	Nd(OC ₁₀ H ₂₁) ₃ 0.098	AlEtCl ₂ 0.147	
35	32	Hexane 1500	205	DIBAH 2.74	Nd(OC ₁₀ H ₂₁) ₃ 0.091	AlEtCl ₂ 0.137	35

40 * TIBA = Al(Buⁿ)₃
** DIBAH = Al(Buⁿ)₂H
*** N.D. = Not Determined

	Polymerization temperature °C	Polymerization time hrs.	Yield %	1,4-Cis %	M _w × 10 ⁻⁵	M _w /M _n	
50	20	5	75	98.0	3.2	3.1	50
55	20	3	89	98.3	4.8	4.6	55
	40	2	68	98.0	3.4	7.0	
60	50	4	93	98.0	2.8	12.3	60
	50	3.5	81	98.2	6.8	12.2	

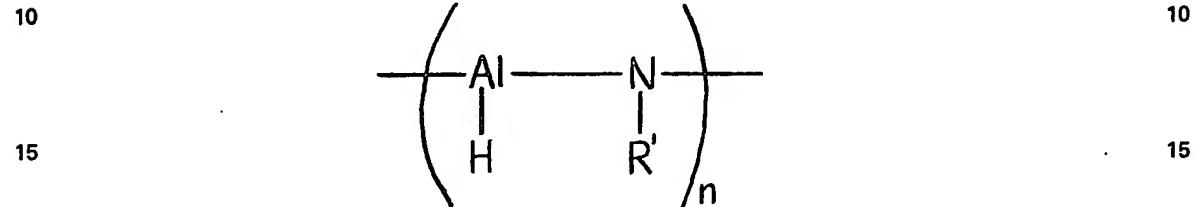
	Polymerization temperature °C	Polymerization time hrs.	Yield %	1,4-Cis %	$M_w \times 10^{-6}$	M_w/M_n	
5	20	3	82	98.9	6.4	N.D.***	5
	50	2.5	74	98.6	10.0	3.6	
10	20	5	96	98.7	15.0	N.D.	10
	20	4	57	98.9	20.0	N.D.	
15	20	7	88	98.2	5.2	14	15
	20	7	85	98.2	4.8	19	
20	20	1.5	80	98.4	5.5	2.7	
	40	2	70	98.0	2.9	5.2	25
25	50	3	81	98.5	5.0	5.6	
	50	3	60	98.6	5.4	7.0	30
30	30	3					

TABLE 5

	Ex.	Solvent mls	Diolefin grams	Component A millimol	Component C millimol	Component B millimol	
35	33	Hexane 4000	570	DIBAH 16.9	$Nd(OBu^n)_3$ 0.26	$AlEtCl_2$ 0.52	40
	34	Hexane 1470	205	DIBAH 2.74	$Nd(O-nC_{10}H_{21})_3$ 0.0914	$AlEtCl_2$ 0.137	
40	35	Hexane 4624	410	TIBA 16.9	$Nd(OBu^n)_3$ 0.26	$AlEtCl_2$ 0.52	45
45							
50							50
55							55
60							60

CLAIMS

1. A catalyst system comprising:
- (A) either (i) an aluminium compound having the general formula RA₁XY, wherein R is a hydrogen atom or 5
a hydrocarbon group containing from 1 to 20 carbon atoms, X is a hydrogen atom, a halogen atom, an alkoxy group, a thioalkoxy group or an amino group, Y is a hydrogen atom, a hydrocarbon group containing from 1 to 20 carbon atoms or a halogen atom, with the proviso that if X and Y are both halogen atoms, R is a hydrogen atom, or (ii) a polymeric aluminium compound having the general formula:



- wherein R' is a hydrocarbon group containing from 1 to 20 carbon atoms and n is an integer;
- (B) a Lewis acid containing at least one halogen atom; and
- 20 (C) a lanthanide compound having a general formula ML_p, wherein M is the lanthanide and L is a monovalent monodentate ligand having the general formula X'R'',_p wherein X' is O, N, S or P, R'' is a hydrocarbon group containing from 1 to 20 carbon atoms, and p is an integer one less than the valency of X'.
2. A system according to Claim 1, wherein the molar ratio of component (A) to component (C) is from 1 to 120.
- 25 3. A system according to claim 1 or 2, wherein the atomic ratio of halogen to lanthanide is from 0.1 to 10.
4. A process for the preparation of a polymer, which comprises polymerising one or more monomers at least one of which is a diolefin in the presence of a catalyst system according to any of claims 1 to 3.
5. A process according to claim 4, wherein the lanthanide content of the catalyst system is from 0.015 x 10⁻³ to 0.5 x 10⁻³ gramatoms of lanthanide per 100g of monomer(s).
- 30 6. A process according to claim 4 or 5, wherein the polymerisation is carried out at a temperature of from -50 to 150°C.
7. A process according to claim 6, wherein the polymerisation is carried out at a temperature of from 10 to 80°C.
- 35 8. A process according to any of claims 4 to 7, wherein the polymerisation is carried out at a pressure of from 1 to 20 atmospheres.
9. A process according to claim 8, wherein the polymerisation is carried out at a pressure of from 1 to 5 atmospheres.
- 40 10. A process according to any one of claims 4 to 8, wherein the polymerisation is carried out in a solvent which is an aliphatic hydrocarbon, an aromatic hydrocarbon, a cycloaliphatic hydrocarbon, or a mixture of two or more thereof.
11. A process according to any of claims 4 to 8, wherein the polymerisation is carried out in the monomer(s).
- 45 12. A process according to any of claims 4 to 11, wherein an aliphatic conjugated diolefin or a mixture of aliphatic conjugated diolefins is polymerised.
13. A process according to claim 12, wherein one or more of 13-butadiene, 1-substituted butadienes, 2-substituted butadienes and 2,3-disubstituted butadienes are polymerised.
- 45 14. A catalyst system according to claim 1, substantially as described in any of the foregoing Examples.
15. A process for the preparation of a polymer, substantially as described in any of the foregoing Examples.
- 50 16. A polymer when prepared by a process according to any of claims 4 to 13 and 15.